UPGRADING OF SOLVENT REFINED COAL

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INTRODUCTION

Several coal liquefaction processes are being developed by various organizations. The initial objective appears to be the production of low-sulfur boiler fuels for power generation, but it is obvious that upgrading of these coal liquids will be necessary to make acceptable quality fuels for home, transportation, and industrial sectors of our economy. Studies have been conducted on the upgrading of coal-derived liquids, tar, and anthracene oil in the past. More recently, Eisen (1) hydrogenated syncrudes from a western Kentucky coal and a Utah coal in an attempt to prepare gas turbine engine fuel. Stein et al. (2) reported their exploratory studies on hydroprocessing of Solvent Refined Coal (SRC), H-Coal, and SYNTHOIL. Several institutions are also stepping up their activities in coal liquids upgrading, as evidenced by a recent symposium (3).

This report presents an evaluation study on hydroprocessing of a blend of 30 weight percent SRC and 70 weight percent SRC process solvent. It was chosen as the feed-stock, because in some respects it is typical of coal liquids such as SYNTHOIL or mixtures of atmospheric bottoms and vacuum bottoms of H-Coal. They have similar boiling point ranges and high percentages of asphaltenes, organic sulfur and nitrogen. The single-stage hydrotreating of the SRC liquid over conventional nickel-tungsten or nickel-molybdenum catalysts does not give very effective hydrogenation even under severe conditions, whereas the hydrogenation effect, as measured by the increase of H/C atomic ratio, N-removal, and S-removal, is substantially improved in the second-stage hydroprocessing of the hydrotreated SRC liquid.

EXPERIMENTAL

The hydroprocessing of coal liquid was studied in a 500-ml magnetically-stirred autoclave. A series of factorial experiments for single-stage hydrotreating of SRC liquid was conducted using Ni-W supported on silica-alumina (Harshaw Ni-4301E) as the catalyst. The feed was a blend of 30 parts SRC solid and 70 parts SRC solvent, with 5 parts of catalyst added per hundred parts of the feed. Ranges of conditions were: temperature 375°-475°C, initial H_2 pressure 600-1,800 psig (to give operating pressure 900-2,900 psig at reaction temperatures), and reaction time 1-4 hours. The autoclave was stirred at 600-700 rpm during the reaction. The reaction time was measured after the autoclave reached the reaction temperature in about 60-70 minutes, and the autoclave was quenched rapidly after the reaction by an internal water cooling coil. Total products were filtered to obtain liquid oils. Asphaltenes and benzene insolubles were determined according to procedures established by the Chemical and Instrumental Analysis Division of the Pittsburgh Energy Research Center (4). Boiling range distributions of selected oil products were obtained by gas chromatography (ASTM D2887). Gaseous products were analyzed by mass spectrometry.

Various commercial catalysts have been tested for comparison. Most catalysts, excepting $ZnCl_2$ and noble metal catalysts, were reduced, sulfided, and crushed to pass through a 60 mesh sieve prior to use.

For a two-stage hydroprocessing, the SRC blend was hydrotreated over a Ni-Mo catalyst (Nalco NM-504), in the first stage, in a 5-liter rocking autoclave. The product was then hydroprocessed over a Ni-W catalyst (Harshaw Ni-4301) in the 500-ml magnetically stirred autoclave. The experimental conditions are described further on.

RESULTS AND DISCUSSION

Single-Stage Hydrotreating. Table 1 shows the design and the results of a series of factorial experiments with three variables of temperature, initial H_2 pressure, and time at three levels. The experiments were carried out in random order. The feed was a blend of SRC solid and SRC process solvent (for the composite analyses, see Table 6), and the catalyst was Ni-W supported on silica-alumina (Harshaw Ni-4301E). The data analysis was made by computer, and the dependence of various measured characteristics (Y), such as conversion of pentane insolubles, C_1-C_4 hydrocarbon yield, S-reduction, N-reduction, oil viscosity, and H_2 consumption on processing variables (X) of pressure, temperature, and time was represented by the following quadratic polynomial

$$Y = \beta_o + \Sigma\beta_i x_i + \Sigma\beta_{ij} x_i^2 + \Sigma\Sigma\beta_{ij} x_i x_j$$

The statistical significance of the regression coefficients (β) has been tested, and it was observed that, except for N-reduction and viscosity, most characteristics correlate well and pass the F-test for fit with 95% confidence. The quadratic approximation yielded plots showing the effects of initial H_2 pressure and temperature on the conversion of pentane insolubles (benzene insoluble + asphaltene) and on S-reduction in Figures 1 and 2, respectively.

Further, this equation can be used to represent characteristic response surfaces during an optimization analysis. The analysis is made by finding an optimum point over the response surface of the characteristic being optimized, while simultaneously keeping other characteristics within specified levels. The main objective of the coal liquids upgrading in the first stage of a two-stage concept is hydrodesulfurization and hydrodenitrogenation. These reactions can be better achieved at higher temperatures, but H_2 consumption and C_1-C_4 hydrocarbon formation could become uneconomically high. Table 2 shows the optimum conditions for (1) achieving a maximum S-reduction while limiting H_2 consumption to 2.8 weight percent (1740 scf/bbl) and C_1-C_4 yield to 5 weight percent, (2) achieving a minimum C_1-C_4 hydrocarbon formation while realizing S-reduction of at least 80% and N-reduction of 35%, and (3) achieving a maximum conversion of pentane insolubles without any characteristic constraints. It appears that temperature is the controlling factor for achieving a desired optimum. Figure 3 shows the change of various characteristics with temperature at an optimum condition of 1,800 psi and 3.18 hours.

Elemental analyses were obtained for some selected oil products. In general, the hydrotreated products were not sufficiently rich in hydrogen, and N and O contents were still too high. The S-removal was relatively satisfactory. Figure 4 shows that the H/C ratio increases only from 0.92 to 1.1, regardless of the increase in H_2 consumption. It appears that, under severe conditions at high temperatures, additional H_2 is consumed in C_1-C_4 hydrocarbon gases formation. The decrease of the N/C ratio is only moderate with rising H_2 consumption.

Various hydroprocessing catalysts (Table 3) were evaluated at one standard set of conditions used in the factorial experiments. The results in Table 4 show that Ni-Mo type catalyst exhibited the best overall activity.

TABLE 1. Factorial experiments - hydrotreating SRC liquid with Ni-W catalyst

Controlled factors			Measured characteristics					
Pressure psi	Temp, °C	Time hr	Pentane insoluble conversion, wt %	C_1-C_4 yield, wt %	% S reduction	% N reduction	Viscosity, cs at 60°C	H_2 Consumed, wt %
600	375	2.5	10.2	0.6	40.9	9.8	113	0.43
1800	375	2.5	23.4	0.9	60.0	19.6	66	1.10
600	475	2.5	-65.6	12.7	63.5	21.0	65	1.16
1800	475	2.5	65.8	13.5	89.6	31.5	4.3	3.76
600	425	1	20.9	2.2	46.1	3.9	58	0.71
1800	425	1	48.6	2.3	72.2	21.7	18	1.69
600	425	4	4.6	6.7	53.0	5.6	33	1.11
1800	425	4	73.7	5.3	86.1	41.3	6.2	3.08
1200	375	1	-3.8	0.4	42.6	7.7	183	0.60
1200	475	1	1.5	10.3	61.7	10.5	45	1.85
1200	375	4	24.5	0.8	60.0	18.2	59	1.18
1200	475	4	8.9	14.8	77.4	23.8	37	2.94
1200	425	2.5	53.7	2.9	73.9	21.0	14	1.51
1200	425	2.5	45.0	3.6	68.7	22.4	14	1.73
1200	425	2.5	50.3	3.7	73.9	21.0	14	1.67

TABLE 2. Characteristic optimization

	Value at maximum % S-reduction	Value at minimum C_1-C_4 yield	Value at maximum PI conversion
Factors			
Pressure, psi	1800	1800	1800
Temperature, °C	429.2	406.4	438.4
Time, hr	3.12	3.18	4
Characteristics			
S-reduction, %	86.4	80[a]	88.8
N-reduction, %	38.0	36.8[a]	38.6
Pentane insoluble conversion, %	80.8	66.7	85.6
C_1-C_4 yield, wt %	5[a]	2.4	7.4
H_2 consumed, wt % (scf/bbl)	2.8[a] (1740)	2.2 (1360)	3.5 (2170)

[a] Limiting characteristics in optimization.

TABLE 3. Hydroprocessing catalysts

Catalyst No.	1 Harshaw Ni-4301	2 Harshaw Ni-4303	3 Harshaw 0402T	4 Harshaw HT-100E	5 Nalco NM-504	6 Girdler T-826	7 Harshaw Pd-0501	8 Linde SK-120	9 Girdler T-309B
Chemical composition, wt %									
NiO	6[a]	6[a]	-	3.8	5.5	2.5	-	-	-
WO_3	19[a]	19[a]	-	-	-	-	-	-	-
CoO	-	-	3	-	-	2.5	-	-	-
MoO_3	-	-	15	16.8	19	10	-	-	-
Pd	-	-	-	-	-	-	0.3	0.5	-
Pt	-	-	-	-	-	-	-	-	0.5
P_2O_5	-	-	-	-	7	-	-	-	-
SiO_2	50	-	5	1.5	1.6	-	-	64.5	-
Al_2O_3	25	75	77	78	64	85	99.7	22.7	99.5
RE_2O_3	-	-	-	-	-	-	-	10.7	-
Physical properties									
Surface area, m^2/g	228	152	200	175	170	232	186	>550	190
Pore volume, cc/g	0.37	0.54	0.4	0.54	0.41		0.38		0.27
Avg. pore diameter, Å	65	142	100	123	97		82		57

[a] Values listed are metal contents of Ni or W.

TABLE 4. Comparative performance of catalysts

(1,800 psi, 425°C, 1 hr)

Catalyst No.	Type	Pentane insoluble conversion, wt %	Bottom (480°C+) conversion, wt %	350°C- yield, wt %	C_1-C_4 yield, wt %	% S reduction	% N reduction	H_2 consumed, wt %	Viscosity, cs at 60°C
1	NiW on silicated alumina	48.6	83.8	58.3	2.32	72.2	21.7	1.69	18.0
2	NiW on alumina	57.4	87.0	58.2	1.70	75.7	21.6	1.88	18.0
3	CoMo on silicated alumina	52.6	85.7	60.5	1.94	63.5	16.7	1.60	21.7
4	NiMo on silicated alumina	60.3	82.5	59.1	1.66	73.9	27.2	2.03	14.5
5	NiMo on P_2O_5-alumina	63.0	83.7	56.6	2.03	77.4	30.0	2.08	13.6
6	NiCoMo on alumina	55.3	87.4	61.4	1.82	68.7	15.3	1.90	19.0
7	Pd on alumina	15.7	91.8	60.7	1.76	28.7	2.0	1.23	54.1
8	Pd on Y-type molecular sieve	24.9	85.0	57.3	2.30	27.0	16.7	1.32	44.2
9	Pt on alumina	12.4	75.2	46.7	1.86	30.4	2.0	1.12	47.6
10	$ZnCl_2$	64.9	86.5	59.1	2.39	37.4	38.4	2.11	10.7
11	None	-10.2	8.2	40.3	1.53	13.0	-	0.40	172

Two-Stage Hydroprocessing. A two-stage hydroprocessing was conducted. In the first stage, the SRC blend was hydrotreated in a 5-liter rocking autoclave at an initial H_2 pressure of 2,200 psi and 415°C for 4 hours. It was judged that this condition would give a good compromise of high S and N reduction with low H_2 consumption and C_1-C_4 yield. The catalyst was Ni-Mo on alumina promoted with P_2O_5 and SiO_2 (Nalco NM-504). The product was then used as the feedstock for a hydrocracking study over Ni-W catalyst on silica-alumina (Harshaw Ni-4301). A series of factorial experiments for this second-stage hydrocracking was conducted at 1,800 psi initial H_2 pressure, with temperature in the range of 377°-433°C and reaction time in the range of 40-180 minutes. The results of the factorial experiments are shown in Table 5. Some results of using catalysts other than Ni-W are also included. Through a computerized regression analysis of the second-stage hydrocracking data, we were also able to determine that most characteristics, such as pentane insoluble conversion, S-reduction, N-reduction, H_2 consumption, and C_1-C_4 hydrocarbon yield, could be represented by the quadratic approximation. Figure 5 shows the change of characteristics with temperature for the second-stage hydrocracking at the specified conditions. It is evident that the upgrading is quite effective at the second stage. The benefit of the second-stage hydroprocessing can be better seen in Table 6, which shows the analyses of products obtained from a two-stage hydroprocessing of the SRC blend. The light fractions (IBP-260°C and 260°-350°C, obtained from a Kontes vacuum distiller) of the second-stage product have very low sulfur and nitrogen contents (pass EPA specifications for turbine oil).

Additional experiments were also made to determine the effect of pressure (Figure 6) in the second-stage hydrocracking. As expected, the hydrocracking effect improved with increasing pressure.

REFERENCES

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(2) T. R. Stein, S. E. Voltz, and R. B. Callen, Ind. Eng. Chem., Prod. Res. Dev., vol. 16, No. 1, 61 (1977).

(3) Symposium on "Refining of Synthetic Crudes," Div. Petrol. Chem., Am. Chem. Soc. Meeting, Chicago, August 1977.

(4) M. J. Mima, H. Schultz, and W. E. McKinstry, PERC/RI-76/6, ERDA (1976).

Reference to a company or brand name is made to facilitate understanding and does not imply endorsement by the U.S. Department of Energy.

TABLE 5. Factorial experiments - second stage hydroprocessing with Ni-W catalyst

(1800 psi initial H_2 pressure)

Temp, °C	Time, min	Pentane insoluble conversion, %	350°C- yield, wt %	C_1-C_4 yield, wt %	% S reduction	% N reduction	H_2 consumed, wt %	Viscosity, cs at 60°C
377	110	22.9	71.7	0.1	44.4	38.2	0.76	7.8
385	60	12.4	67.5	0.1	22.2	30.2	0.58	8.2
385	160	38.3	65.6	0.1	55.6	41.9	0.94	6.7
405	40	9.8	61.5	0.1	66.7	33.7	0.58	7.5
405	110	41.4	58.7	0.4	44.4	47.7	0.91	6.1
405	110	33.9	71.8	1.1	44.4	54.7	1.00	6.1
405	110	42.1	62.7	1.0	33.3	55.8	1.13	6.1
405	180	41.8	69.9	1.1	66.7	61.6	1.35	5.0
425	60	45.7	65.8	1.2	55.6	46.5	0.85	5.3
425	160	56.6	66.8	2.0	55.6	66.3	1.70	3.6
433	110	55.5	64.9	2.1	44.4	59.3	1.55	3.7
Catalyst effect								
425[a]	160	60.4	65.0	1.94	66.7	51.2	1.47	3.7
425[b]	160	10.5	64.9	2.29	55.6	74.4	1.87	3.5
425[c]	160	51.2	70.3	1.96	55.6	34.9	1.10	4.4

[a] Co-Mo on alumina, Girdler G-51.
[b] Pd on molecular sieve, Linde SK-120.
[c] Pt on alumina, Girdler T3093.

TABLE 6. Two-stage hydroprocessing of SRC liquid

	SRC[a] blend	First-stage[b] hydroprocessed product	Second-stage[c] hydroprocessed product			
			Overall	IBP-260°C	260°-350°C	350°C+
Composition, wt %						
Oil	69.50	93.8	96.7			
Asphaltene	19.58	6.1	3.3			
Benzene insol	10.92	0.1	-			
Fraction, wt %						
IBP - 260°C	5.93	21.92	29.54			
260°C - 350°C	17.70	39.74	45.19			
350°C +	76.36	38.34	25.28			
Elemental analysis, wt %						
C	88.19	89.20	89.29	88.46	89.93	90.31
H	6.78	8.47	9.36	11.13	9.46	8.00
N	1.43	0.84	0.51	0.04	0.11	0.75
S	0.58	0.10	0.049	0.035	0.048	0.113
O	2.89	1.39	0.79	0.34	0.55	0.82
Ash	0.13	-	-	-	-	-
H/C atomic ratio	0.92	1.20	1.26	1.51	1.26	1.06
Specific gravity, 15/15°C	1.122	1.023	0.980			
Viscosity, cs at 60°C	450	39.8	5.0			

[a] SRC blend contains 30 parts SRC solid and 70 parts SRC solvent.
[b] Hydroprocessed at 1800 psi, 415°C and 4 hours with Ni-Mo.
[c] Hydroprocessed at 1800 psi, 405°C and 3 hours with Ni-W.

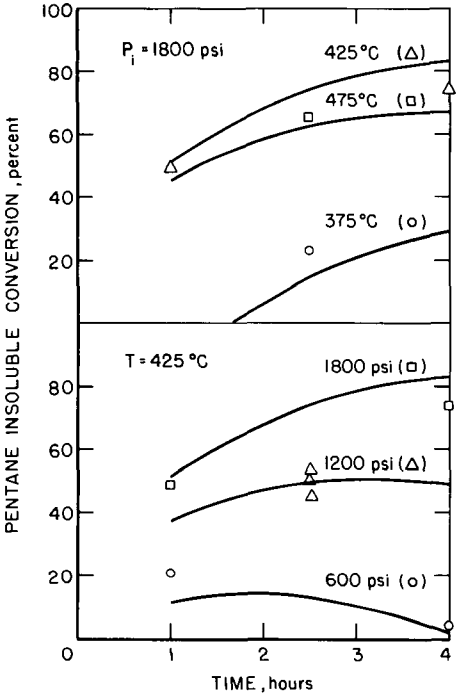

Figure 1-Effects of pressure and temperature on pentane insoluble conversion.

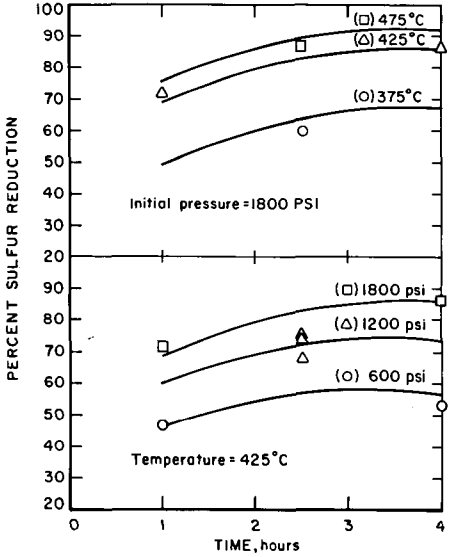

Figure 2-Effects of pressure and temperature on sulfur reduction.

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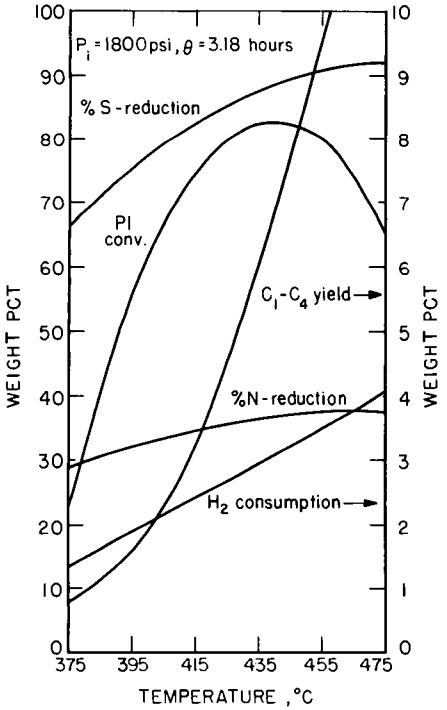

Figure 3 - Chonge of characteristics with temperature .

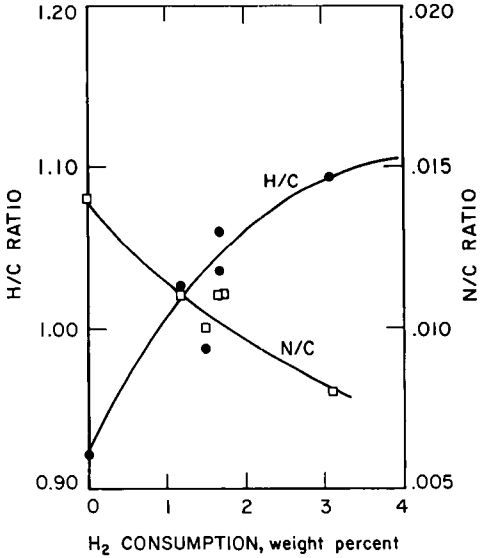

Figure 4 - Change of H/C ond N/C ratios with H_2 consumption.

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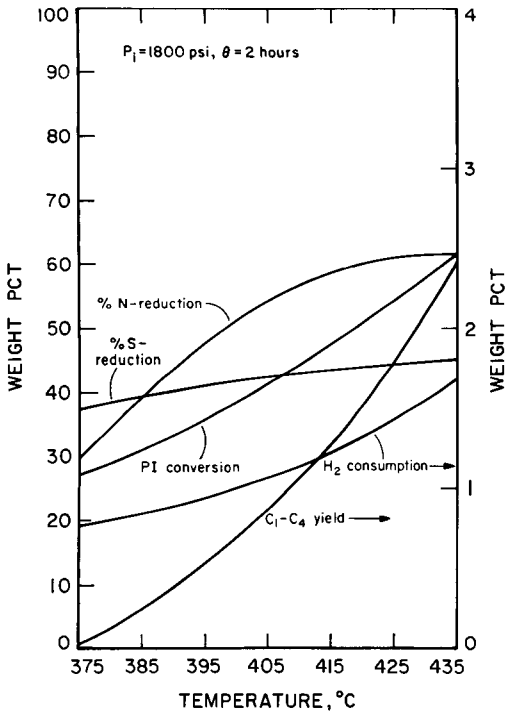

Figure 5–Change of characteristics with temperature for second-stage hydrocracking.

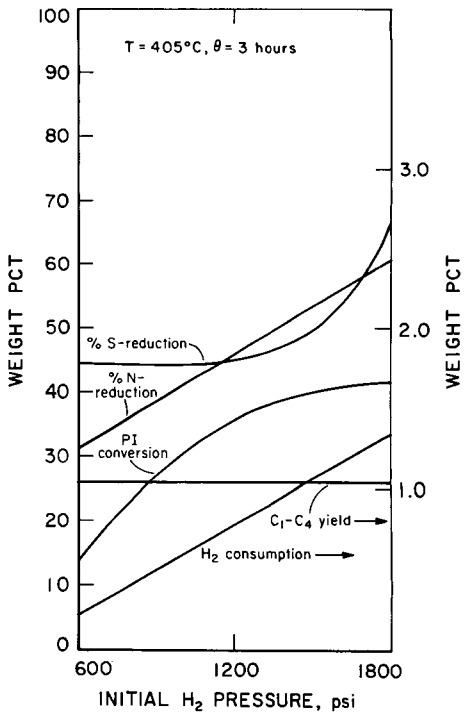

Figure 6–Effect of pressure in second-stage hydrocracking.

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